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REPORT DOCUMENTATION PAGE			READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER AFOSR-TR-81-0531	2. GOVT ACCESSION NO. AD-A101039	3. RECIPIENT'S CATALOG NUMBER		
4. TITLE (and Subtitle) Mercury Cadmium Telluride Sputtering Research	5. TYPE OF REPORT & PERIOD COVERED Annual Technical Report			
7. AUTHOR(s) Roy H. Cornely	3	6. PERFORMING ORG. REPORT NUMBER		
9. PERFORMING ORGANIZATION NAME AND ADDRESS New Jersey Institute of Technology 323 High Street Newark, New Jersey 07102	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 11C2			
11. CONTROLLING OFFICE NAME AND ADDRESS Electronic and Solid State Sciences Div AFOSR Bldg. 410, Bolling Air Force Base Washington, D. C. 20332	11a. REPORT DATE 11b. NUMBER OF PAGES 16			
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) LEVEL	15. SECURITY CLASS. (of this Report) Unclassified			
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	15e. DECLASSIFICATION/DOWNGRADING SCHEDULE			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)	SELECTED S JUL 1 1981			
18. SUPPLEMENTARY NOTES				
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Mercury Cadmium Telluride, Semiconductor Thin films Prepared by rf Triode Sputtering, Optical and Electrical Properties of Mercury Cadmium Telluride Thin films.	342024			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A large number of 5-10 micron thick n and p-type films on Si and CdTe substrates were prepared by Hg vapor rf triode-sputtering using pressed-powder targets. The targets had different percentages of CdTe particles and thus films with the CdTe mole percent (x values) between 0.18 and 0.27 were obtained. It was demonstrated that the grain size and mobility of the sputtered polycrystalline films, with a high degree of (111) crystal orientation, could be greatly increased by annealing the films at 553-623 degrees Kelvin in a Hg atmosphere. For example,				

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$x = 0.27$ films had as-sputtered electron mobilities less than 20 percent of ideal bulk-crystal material at 300 degree Kelvin and less than 4 percent at 85 degree Kelvin with free electron concentrations 20 times intrinsic material at 85 degrees. After annealing at 553 degrees in 74 mm pressure of Hg, the electron mobilities were 71.5 and 16.5 percent of ideal values at 300 and 85 degrees respectively with carrier concentrations in the 10 to the sixteenth per cubic cm range. Similar results were obtained using CdTe and Si substrates and for other compositions. For films with 0.18 CdTe mole percent, electron mobilities of 24,000 cm squared per volt second were measured at 85 degrees. Two step annealing processes, with separate temperatures for grain size enlargement and stoichiometry adjustment, and low temperature heat treatments for preventing peeling by grading the Si-(Hg,Cd)Te interface appear necessary for further optimization of the annealing effects.



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2.0 Research Report

2.1 Film Deposition Experiments

Twenty film deposition sputtering runs were made between July 1980 and April 1981. Six of these runs were aborted because of either vacuum leaks or sputtering through the target to its backing plate. The main purpose of the deposition runs was to obtain a large number of 5 to 10 micron thick films (with relatively good crystallinity) on high resistivity (100-1000 ohm-cm) silicon substrates with (111) surface orientation. These samples were annealed under various conditions to find optimum annealing parameters. The films has typical room-tempearture electron mobility values of about 1000 cm² per volt/sec. as shown in table I, at the end of section 2.6. Thus the deposition work did not concentrate on further optimization of sputtering parameters but rather demonstrated that the electrical parameters of $x = 0.25$ and $x = 0.18$ material sputtered on silicon substrates were reproducible for the sputtering parameters used. Recent research has indicated ways to improve these as-deposited film properties.

In each successful deposition run about six films were deposited through a metal mask so that they had the Hall-effect, clover-leaf geometry with the central region (whose properties are measured) being 3.1 mm in diameter. About three samples were of large area (about 1 cm²) for compositional measurement by optical absorption. Because of the expense of single crystal CdTe substrates with (111) surface orientation (~\$150 for a 1 cm square substrate) only one or two CdTe substrates were used in each deposition run. The main deposition parameters were: r.f. power applied to the target, 125 watts or 4.87 watts/cm²(+5 percent), target compositional parameter $x = 0.25, 0.23,$ or $0.18;$ mercury sputtering pressure, 1 to 2 microns; deposition rate, about 1 micron per hour; and substrate temperature, 250 to 300°C. The targets used were 5.7 cm in diameter, with an area of 25.5 cm², and 0.15 to 0.3 cm thick. Exact values of the key sputtering parameters used for the films whose as-deposited electrical properties are reported here are given in table I. It should also be mentioned that with a film thickness of 5 to 10 microns it is difficult to measure the thickness with better than fifty percent accuracy using interferometry because of the large number of fringes. Therefore, measurement of film thickness by more time consuming scanning electron microscopy (SEM) is necessary for very accurate measurements. These measurements were made at NJIT on many samples whose characteristics are of particular interest, but this measurement work has not yet been tabulated. Exact thickness values are required to obtain deposition rates so that the sensitivity of deposition rate on crystallinity and other film properties at fixed substrate temperature and Hg pressure parameters can be determined.

2.2 Structural and Electrical Properties of As-Deposited Sputtered Films.

A large number of films sputtered on silicon substrates were tested for crystallinity, composition, and electrical properties. The SEM and

x-ray diffraction measurements continued to show that the as-deposited films, although polycrystalline with grain boundaries perpendicular to the surface, have a strong preference for (111) crystal orientation. In fact, as previously reported by this laboratory(1), films deposited at about 1 $\mu\text{m}/\text{hr}$ deposition rates with substrate temperatures in the 200-300°C range had nearly complete (111) crystal orientation; that is, orientations present to a strong degree in finer grain films such as the 311, 220, 331, and 642 were not appreciably present. Figures 1 and 2 show x-ray diffractometry patterns for as-deposited films with 100 percent and nearly 100% (111) crystal orientation. In figure 1a, the gain of the x-ray electronics is set so that the full (111) peak is observed. In 1b, the scale is amplified so that other peaks are observed; only the small 422 and 553 peaks are not multiples of (111) crystal orientation diffraction. In figure 1c, the (444) peak is amplified to its maximum since its width is believed to be indicative of the crystallite size. Figure 2 shows results for a film with strong (111) orientation but with other non (111) crystal orientations also appearing. The (444) peak in (2c) is seen to be broader than for the film in figure 1. A correlation between the "background" of small peaks associated with non (111) crystal orientations and the width of the (444) peak with the crystallite size as indicated by Hall-effect, mobility measurements and SEM surface morphology studies is being made.

New results have not been obtained on the crystallinity of the sputtered films since those reported in the November, 1980 AFOSR proposal and in reference 2. NJIT plans to examine again the surface morphology and crystallinity of films with the best electrical results in the summer of 81.

The key deposition parameters of films deposited on both CdTe and Si substrates that yielded typical as-deposited electrical properties are given in Table I placed at the end of section 2. The rf power applied to the target for these films was kept constant at about 125 watts or 4.87 W/cm² (± 5 percent). This power setting yields films with deposition rates of about one micron per hour. Also shown in this table are electron mobilities and carrier concentrations at room temperature obtained by Hall-effect measurements on samples with the clover-leaf Hall-effect geometry and 3.1 mm diameter central region. These results, reported in reference 2, are typical values for the films deposited in the 80-81 grant period.

2.3 Annealing Procedures and Properties of Annealed Films.

A major effort was made during this grant period to improve film properties by post-deposition annealing. Thirty one annealing runs were made. Samples to be annealed were mounted in pairs on a quartz fixture placed at the end of an 18 mm ID - 21 mm OD quartz tube. A small pool of Hg was placed in the tube 11 cm from the samples and the tube pumped down to a pressure of about 1×10^{-5} torr and then sealed off. Samples were then annealed in a two-zone furnace, with the temperature of the cold end determining the Hg pressure over the heated coated wafer. Table II lists the annealing parameters and conduction properties obtained for some of the samples listed in Table I. Table II was published in reference 2. In the course of obtaining experience on how to anneal (Hg,Cd)Te films on Si and CdTe substrates, about ten samples

were destroyed due to the film peeling from the substrate. This problem was alleviated by slowly raising the temperature to the anneal value (in 7.5 hours for the samples in table 2). For the samples in Table II, the temperature was also slowly decreased from the anneal value. Results are presented for samples annealed for 40 hours on CdTe substrates as well as Si substrates and for the two extremes in composition that were studied. It was recently found that films annealed at 280°C could be rapidly quenched without harmful effects such as peeling and loss of Hg from the film.

The sensitivity of annealing results to Hg pressure is illustrated by the values in the table for the first two annealing runs where the film numbered 1 was annealed first with 17.3 mm and then 24 mm of Hg pressure. After the first anneal, the film showed behavior dominated by acceptor-like vacancies. After the second anneal, the film was n-type with an electron mobility 67 percent of high-quality, bulk material. The mobility at -188°C increased to only 11 percent of bulk material mobility. (The bracketed numbers are the minimum values for single crystal bulk material considered to be of high quality). Similar results were obtained for films 2 and 4 which were annealed with higher Hg pressure, i.e., 74 mm, which resulted in somewhat higher carrier concentrations. A decrease in the Hg pressure from 74 and 33 mm for the second anneal of film 4 did not appreciably lower the carrier concentration. These results suggest that the Hg pressure is excessive, i.e. the electron concentration is due to interstitial Hg. However, when the Hg pressure is lowered as for the case of film 1, compensated material results with mixed conduction due to acceptor-like levels probably due to cation vacancies. Note that the results for film 6 on a Si substrate are similar to the results for films 1, 2 and 4 on CdTe substrates. (The mobility value at -188°C for film 6 was extrapolated from other low temperature data as the sample was broken during the measurements.)

The results for annealing experiments with $x = 0.18$ thin films were also informative. In the case of the first annealing experiment with film 9, very high carrier concentrations were obtained even though the Hg pressure was low (i.e. 0.27 mm). An increase of the Hg pressure to 17.3 mm (along with an increase of the substrate temperature to 350°C to promote grain growth) resulted in a film with a mobility value at -188°C that is 16 percent of ideal material. [Note that the film is only 5 μm thick and on a Si substrate.] The carrier concentrations for this film and the similar film 17 are lower than for the $x = 0.27$ films.

2.4 Discussion of Electrical Properties

Hall-effect measurements on the as-deposited films point out the sensitivity of the film structure and defect concentration to the sputtering parameters, particularly substrate temperature and Hg pressure. With further experimental work the composition and grain size can probably be controlled to yield as-deposited properties considerably improved over those obtained so far even though the sputtering process is quite complex in terms of control of atomic transport in the target, through the plasma, and at the substrate. It was shown that, by simply changing the x -value of a pressed-powder target, films with an x -value close to, if not the same as, the x -value of the target can be prepared in the compositional range of $0.1 < x < 0.27$. Further work is necessary to measure the exact composition of the films and to correlate the Burstein-Moss shift at 300K with electron carrier concentration. The fact that the as-sputtered film mobilities are less than 0.1 percent of ideal

2.5 Film Compositional Analysis Work

Composition of the sputtered films is being measured by three methods: 1) Determination of the optical absorption edge (which is related to the average composition through the film) by infrared spectrophotometry and 2) ESCA (electron spectroscopy for chemical analysis) measurements which yield the composition within the first 10 \AA of a film surface. With most materials, Ar $^+$ sputtering is used to remove slices of material to obtain in-depth compositional profiles. However, in the case of (Hg,Cd)Te, NJIT found that Hg tended to be depleted from the surface with Ar $^+$ sputtering. This was confirmed by a recent publication(4) that reported a) changes in the stoichiometry of HgTe and (Hg. x Cd. $_{1-x}$)Te surfaces due to Ar $^+$ and b) when CdTe was Ar $^+$ sputtered the CdTe surface maintained perfect unreconstructed stoichiometric composition. Therefore, in-depth compositional profiling must be done by slow, well controlled chemical etching procedures that remove 100 to 200 \AA slices of (Hg,Cd)Te material. NJIT has been doing research on low temperature (dry ice) etching using methanol solution containing less than one percent of bromine. This work which involves high magnification SEM is being done as part of the target research sponsored by the ARO grant and is necessary for obtaining the concentration profile of Hg, Cd and Te atoms into the target during Hg $^+$ sputtering. 3) Electron Microprobe Analysis (Wavelength Dispersive Spectroscopy -WDS). Standard pieces of (Hg,Cd)Te with thirteen different known compositions were kindly lent to NJIT by J. Schmidt of Minneapolis Honeywell Corporation. Five of these samples (with $x = 0.320, 0.245, 0.217, 0.212$, and 0.165) were measured by WDS at Structure Probe Inc. (without informing them of the values Honeywell had obtained by several measurement methods). Structure Probe was able to determine the values with an average accuracy of better than one percent after calibrating their WDS equipment using a CdTe standard and a standard with $x = 0.205$ provided by Peter Brott of Hughes, Santa Barbara. This is an encouraging result that will enable NJIT to compare the composition of the films with that of the target and with that indicated by optical absorption data.

Figure 3 shows typical absorption coefficient data (published in reference 2) obtained from dual-beam optical transmission measurements of films deposited using physical mixture targets with x values of 0.10, 0.18, 0.20 and 0.25. Much effort was put into making optical transmission measurements on a large number of samples. This task is difficult when the Si substrate is thicker than 10 mils. The data in figure 3 are compared with accepted experimental data for bulk material with x values of 0.14, 0.21 and 0.25[11] (There is a paucity of published absorption coefficient data for bulk material, particularly with known free carrier concentrations.) Although the absorption edge for the sputtered films is not as sharp as for the calculated curves for ideal material, it is sharper than for the bulk crystal data probably due to better compositional uniformity. Also shown in the figure are calculated absorption coefficient curves for $x = 0.10, 0.18, 0.20$ and 0.25 compositions using equations recently derived for (Hg,Cd)Te material.[12] The calculated curves used experimental gap values of 0.24, 0.136, 0.162, and 0.228 [eV] from [13] for $x = 0.10, 0.18, 0.20$ and 0.25 compositions respectively and assumed pure, intrinsic material, that is no Burstein-Moss shift [12]. It is seen that the location of the absorption edge for the sputtered films is in fair agreement with the calculated data for ideal material. We have found that the absorption edge for sputtered films is usually shifted toward higher energies from the calculated curves as in the case of the curves in figure 3 which are for films similar to the n-type films in Table I, with carrier concentrations in the high 10 17 cm $^{-3}$

material values at 23°C and less than 3 percent at -188°C with relatively high carrier concentration values shows that the films contain more defects than desired. Optimization of defect concentrations at lower substrate temperature should be attempted since it has been reported that substrate temperatures of 150°C yield optimum results in D.C. triode-sputtering of $(\text{Hg}_{.8}\text{Cd}_{.2})\text{Te}$ films on CdTe substrates.(25) Substrate temperatures of 150°C were originally tried in this research but films on Si substrates were found by x-ray diffraction to have non-oriented grains with a mixture of (111), (311) and other crystal orientations. With additional substrate surface preparation, such as the use of graphoepitaxial techniques, this problem can probably be minimized. Also the smaller grain size for films sputtered on Si substrates at 150°C could be enlarged by high temperature annealing in Hg atmosphere. Another parameter that must be more extensively studied is the deposition rate. Recent results show an improvement in film quality by reducing the rate from 1 to 0.5 $\mu\text{m}/\text{hr}$.

The Hall-effect results obtained with films annealed in a Hg atmosphere in a 2-zone furnace were encouraging. For the $x = 0.27$ films on CdTe substrates, mobility values of up to 71.5 percent of high-quality single-crystal material were obtained at 23°C and up to 16.5 percent at -188°C. However, the measured carrier concentrations indicate that the defect levels were high, probably due to cation vacancies. [The mobility values for films on Si substrates were not much lower although difficulty with thermal stress was encountered if the annealing temperature was not slowly increased]. From the experimental results, it appears that significant improvement in the electron mobility and carrier concentration values would be obtained if the cation vacancies in the as-deposited films were minimized and if the Hg pressure for annealing the films optimized. A two-step annealing process-one step at a high temperature of about 350°C to remove grain boundaries and a second step at a temperature of about 280°C to minimize defect levels-would appear to be desirable.

The results for $x = 0.18$ films were similar to those for the $x = 0.27$ films in that the mobility values at 23°C and -188°C were 56.7 and 16 percent, respectively, of the values for high quality single-crystal material. It is expected that the mobility is lower by a factor of 2 to 4 due to surface scattering for films only 5 μm thick. The mobility is also lowered by the defect level which appears from the carrier concentrations to be lower than in the $x = 0.27$ films. It is also expected that a second anneal at about 280°C with about 17 mm of Hg pressure could decrease the vacancy defect level which was probably increased by the 350°C anneal. This second anneal could lower the carrier concentration by a factor of at least 10 and increase the lateral mobility. However, it is possible that the best 0.18 films obtained by annealing are already of device quality especially if the devices require current to flow parallel to the grain boundaries and perpendicular to the film surface, as in the case of photovoltaic devices. Additional research, including completion of minority carrier lifetime measurement at -188°C, and actual device testing must be done to completely determine the value of the sputtered films. It is possible that films with mobilities less than those obtained in high-quality single-crystal material may be ideal for certain devices such as short-length photoconductors due to phenomena such as the carrier sweep-out effect (3).

range. The shift could be due to the x value of the film changing from that of the target due to cadmium enrichment; however, it is more likely due to the Burstein-Moss shift due to high electron concentration in the films since p-type films have been found to lie generally closer to the calculated curves. A more complete study of the absorption edge shift as a function of film carrier concentration for films with composition measured by wavelength-dispersive electron microprobe analysis is now being done at NJIT.

2.6 Laboratory Equipment Work

Numerous practical tasks were completed during this grant. Some of these tasks are listed below.

- 1) The triode sputtering equipment, with the Hg diffusion pump and container with liquid Hg, that is used for (Hg,Cd)Te film depositions was maintained and repaired by students using a helium leak detector, fresh air masks, and other accessory equipment. An improved target mask system, with more reliable mechanical fixtures, was designed and built. The water system for cooling the anode, triode filament, and target assemblies was redesigned so that the water could be heated preventing Hg from condensing when a Hg pressure above one micron was required.
- 2) A 2-zone annealing furnace was purchased in the spring of 1980. Work was done to obtain the temperature profile of the furnace at various control settings so that Hg pressure could be maintained independently of the substrate annealing temperature. It was found that the Hg pool and substrate could be positioned 11 cm apart and still maintain a temperature difference up to 300°C. Settings were found for maintaining separate temperatures in the 150-350 degree range.
- 3) The laboratory setup for making minority carrier lifetime measurements of (Hg,Cd)Te films over the 80 to 300°K temperature range was designed and constructed in the summer of 1980 and some preliminary measurements taken. It consists of a cold frame in a vacuum system onto which samples can be mounted. The laboratory setup is described in detail in the Nov. 1980 proposal.
- 4) The four point probe, van der Pauw Hall-effect sample holder is sealed off in a vacuum of about 10^{-3} torr and using a thin wall dewar it can be cooled down to 80°K in about 5 minutes. The sample holder was recently redesigned so that two samples can be tested during one vacuum pumpdown. The new design also puts less probe pressure on the sample and allows for easier probe motion for different contact geometries.
- 5) A second (backup) thermal evaporation system was made operational for contact evaporation work.

Table I Deposition Parameters and Hall-Effect Data for As-Deposited Films

Film No.	x-value	Deposition Parameters			Hall Effect Data Before Annealing		Low Temperature (-188°C)	
		Deposit Time [Hrs]	Mercury Pressure [mm]	Cathode Voltage [volts]	Substrate Temp. [°C]	Room Temperature Mobility [cm²/volt-sec.]	Carrier Concent. x10⁻¹⁶ [cm⁻³]	Mobility [cm²/volt-sec.]
1-CT	.27	8	7	1600	250	1045	61	1727
2-CT			↓	↓		1001	67.5	1656
3-Si			↓	↓		721	12.6	852
4-CT			5	1700		615	8.65	122
5-Si						678	7.5	241
6-Si	↓		↓			958	6.6	434
7-CT	.2	.9				922	26.3	1372
8-Si						1159	17.1	1527
9-CT						1051	28.7	1507
10-Si	↓		↓	↓		1115	10.9	1781
11-Si	.18	1.2	2250			689	15	97
12-Si			↓	↓		1110	7.1	237
13-Si		1.4		↓	↓	561	3.3	527
14-Si		1.8-2.0	2400	300		870	1.2	1100
15-Si						400	0.83	370
16-Si	↓	↓		↓		700	3.1	340
17-Si	5	1.4		250		1300	35	1920
18-Si	↓	↓	↓	↓		1000	40	1400

Table II Annealing Conditions and Hall-Effect Data for Annealed Films

Data in Parentheses are As-Deposited Values from Table I. Data in Brackets are Values for Bulk Crystals

Film No.	Annealing Conditions				Hall Effect Data After Annealing			
	Film Thick [μm]	x-value	Substrate Temp. (°C)	Mercury Pressure (mm)	Room Temperature Mobility [cm²/volt-sec.]	Carrier Concent. x10⁻¹⁶ [cm⁻³]	Low Temperature (-188°C) Mobility [cm²/volt-sec.]	Carrier Concent. x10¹⁶ [cm⁻³]
1-CT	~8	.27			(1045)	(61)	(1727)	(66)
1-ET	↓	1	280	17.3	514	3.5	33	21
1-CT	↓		280	24	3487	8.3	5473	3.6
2-CT	-8				[5200]	[0.4]	[50,000]	[0.2]
2-CT			280	74	(1001)	(67)	(1656)	(75)
3-CT			280		3799	38	7663	36.5
4-CT			280	74	(615)	(8.6)	(122)	(4.4)
5-Si			280	33	3722	28	8277	29
6-Si		↓	280	24	3699	19	6717	19
7-CT		.18			(958)	(6.6)	(434)	(2.5)
7-CT	↓		280		3905	11.1	7000	—
8-Si	5.1				(1051)	(29)	(1507)	(25)
10-Si	5		280	27	1945	195	7132	183
10-Si	↓		350	17.3	(1000)	(40)	(1400)	(40)
12-Si	5		350	17.3	8500	3.4	23,800	5.4
12-Si	↓	↓	350	17.3	[15,000]	[3]	[150,000]	[10.1]
17-Si	5				(1300)	(35)	(1920)	(34)
17-Si	↓				10,000	22	12900	18

Figure 1. The x-ray diffraction trace of the sample T28Si. (a) Normal magnification used to calculate the percent preferred orientation, (b) Amplified x-ray trace to show all orientations, (c) Actual size of (444) peak using highest magnification.

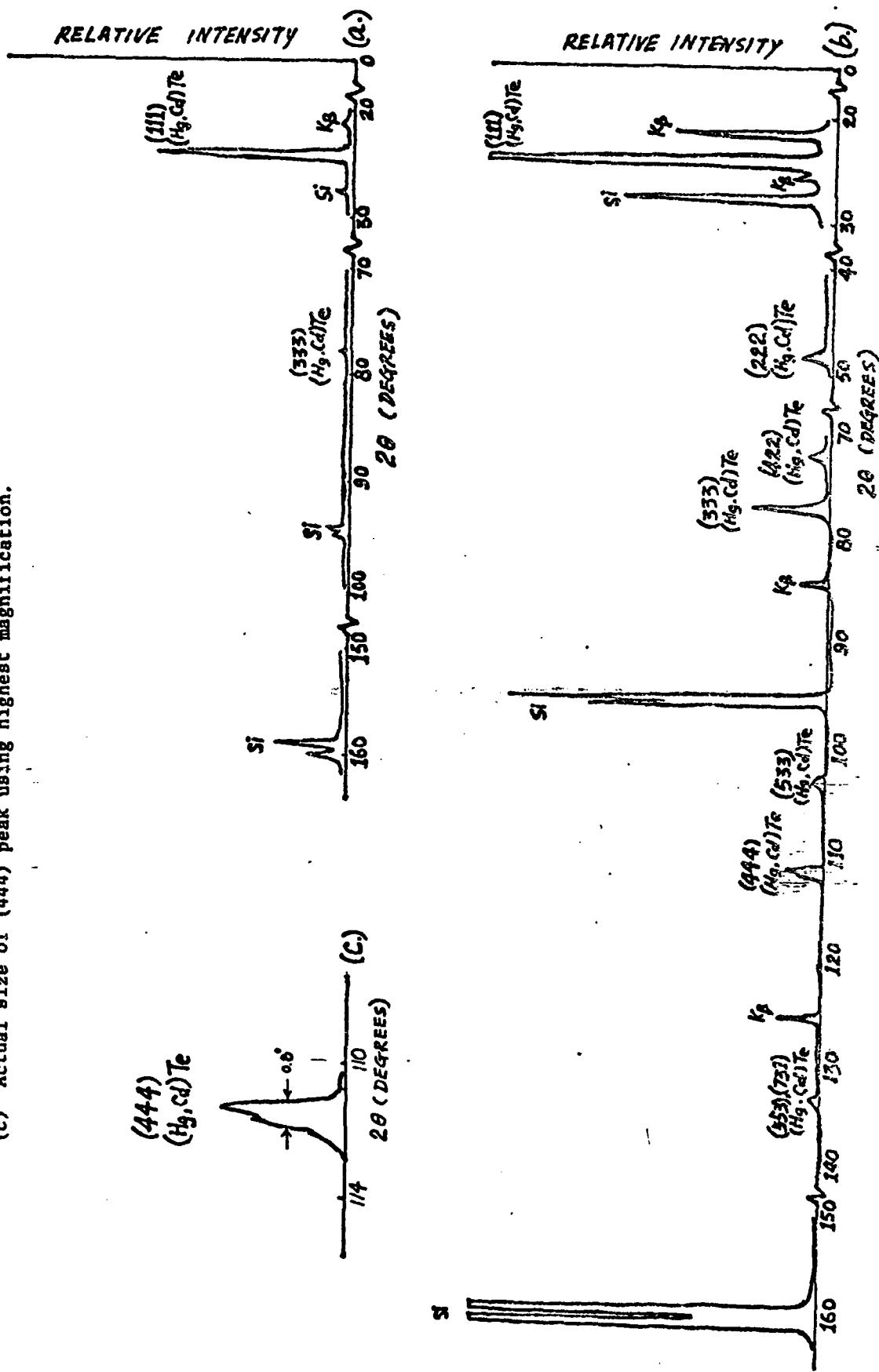
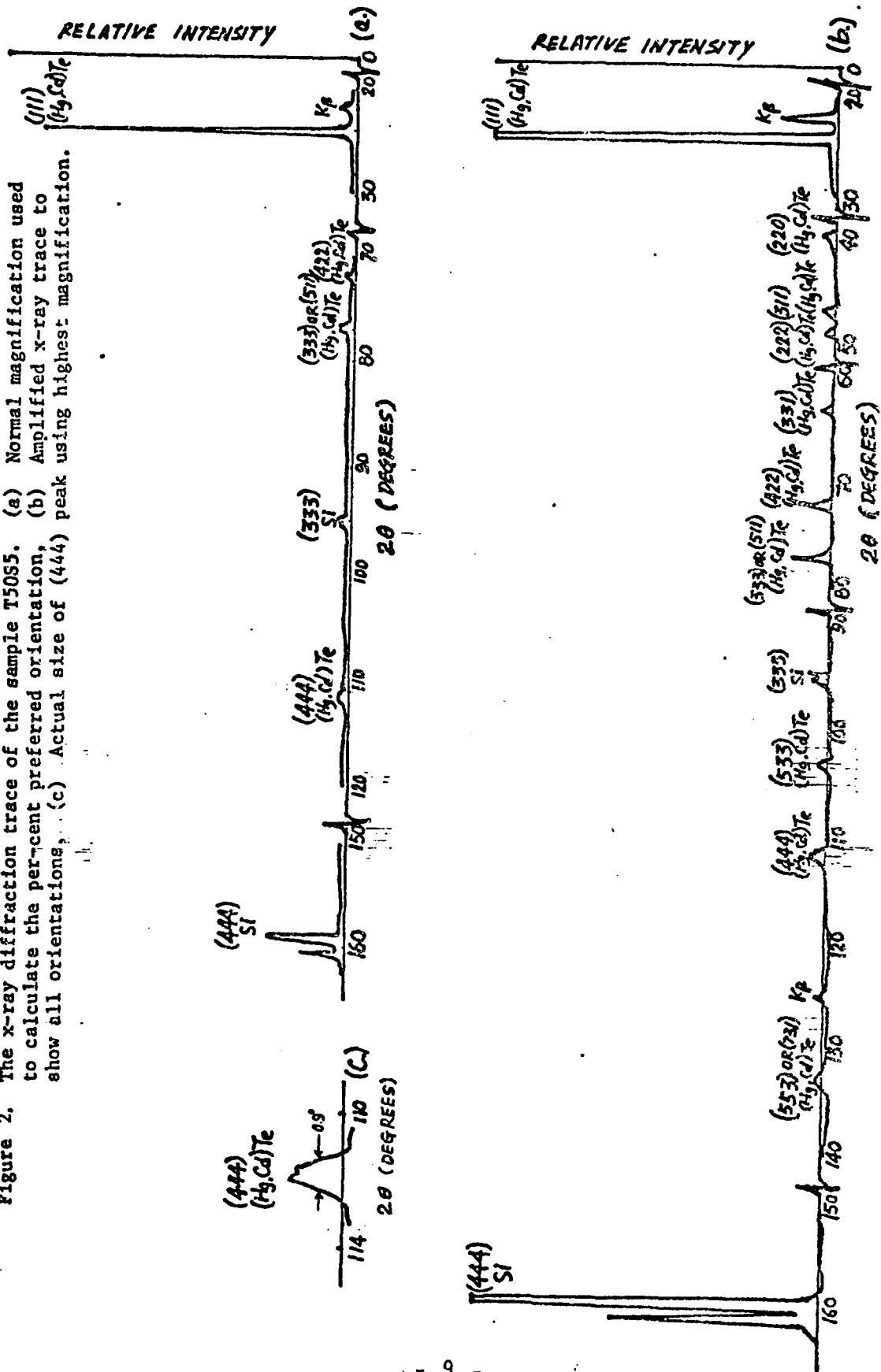


Figure 2. The x-ray diffraction trace of the sample T50S5. (a) Normal magnification used to calculate the percent preferred orientation; (b) Amplified x-ray trace to show all orientations; (c) Actual size of (444) peak using highest magnification.



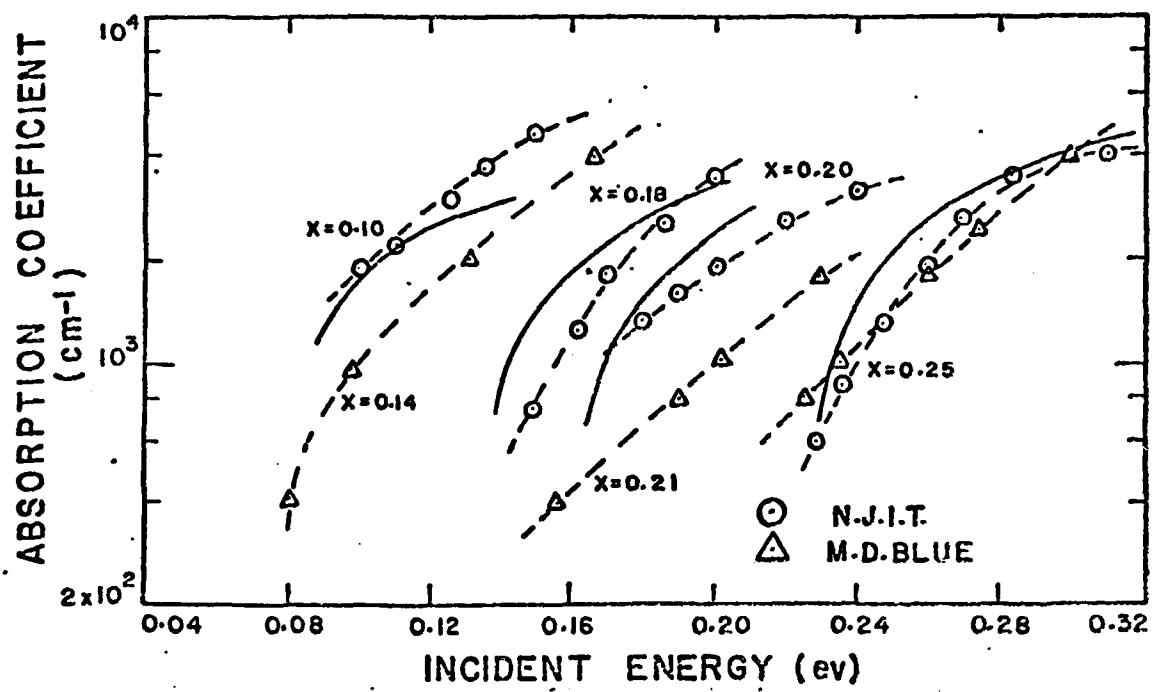


Figure 3. Absorption coefficient of sputtered thin films and bulk-crystal material versus incident energy. [Solid curves are calculated values based on reference [12]].

3.0 Summary and Future Plans

To achieve the overall objective of developing thin film process for manufacture of high-quality, low cost, thin film $(\text{Hg}_{1-x}\text{Cd}_x)\text{Te}$ material on low cost, electronically active substrates, NJIT has worked in four research areas - simultaneously. These areas were measurement and analysis of film properties and optimization and control of sputter-deposition, post-deposition annealing, and target fabrication parameters. Significant progress was made in each of the four areas for $(\text{Hg}_{1-x}\text{Cd}_x)\text{Te}$ compositions ranging from $x = 0.18$ to $x = 0.25$. Evidence of this progress was presented in previous sections of this annual report. Particularly, the relatively high mobility ($\frac{1}{5}$ of bulk crystal mobility) obtained at 80°K , even with 10^{16} cm^{-3} donor concentration due to excessively high Hg pressure used during annealing, showed that fairly high quality $(\text{Hg},\text{Cd})\text{Te}$ thin films can be obtained on silicon substrates. It appears certain that with further research high quality films can be reliably obtained using post-deposition two-step annealing techniques. One task is to find the lowest annealing temperature and shortest time at which the grain boundaries in the as-sputtered polycrystalline films can be removed. A good starting temperature is 350°C , at which temperature the best annealing results were obtained, although higher temperatures may be necessary. At this temperature, even in a Hg atmosphere, additional defects will form. Therefore, the second task is to find the optimum temperature and Hg pressure for the second step anneal. This anneal will be used to adjust the film stoichiometry to obtain the lowest possible n-type carrier concentration thus assuring a high-quality photoconductive material.

Optimization and control of sputtering parameters, particularly Hg pressure, substrate bias and temperature, and deposition rate, could allow for high quality films to be made even without using annealing processes, particularly if higher-cost CdTe substrates or thin-film layers are used. Deposition rates of $0.5 \mu\text{m}/\text{hr}$, about one half of the rate used for most of NJIT's deposition runs, have been reported by French researchers⁽⁵⁾ to yield high quality films on CdTe substrates using pressed-powdered targets in a triode sputtering system. Because of the large number of deposition and annealing parameters whose optimum values vary with film composition, NJIT plans to make films in the near future with just one target composition, $x = 0.2$. Concentration on optimization of the deposition and annealing parameters for a single composition should enable high quality films to be obtained in a shorter time.

NJIT proposed and has initiated work in a fifth area of $(\text{Hg},\text{Cd})\text{Te}$ thin film research-substrate surface preparation-that should enhance the probability of obtaining high-quality, as-deposited films on Si substrate and also lead to interesting scientific results. The proposed research is based on research on grapho-epitaxy at MIT's Lincoln Lab that showed that by introducing regularly-spaced nucleation centers, or lines with sharp changes in geometry (such as saw-tooth structures), the crystal size of a deposited film on an amorphous substrate can be greatly enhanced. These lines can be introduced by etching [with an anisotropic etch^[6,7]], sawtooth structures with (111) surfaces-ideal for $(\text{Hg},\text{Cd})\text{Te}$ into Si with (100) surface orientation. Although the Lincoln Lab research has concentrated on deposition of single crystal material (particularly silicon) on amorphous (e.g. glass) substrates⁽⁸⁾, some promising results have been obtained with Ge deposited on Si substrates.⁽⁹⁾ Some preliminary research was completed during this grant on grapho-epitaxy applied to $(\text{Hg},\text{Cd})\text{Te}$ growth.

Three samples with sawtooth structures and four micron periodicity were sent to NJIT from Lincoln Lab by Dr. M. W. Geis of Lincoln Labs on November 3, 1980. One sample was over-etched with rounded tops, one sample was under-etched with a flattened top covering about 30% of a period, and the third sample was an unetched control sample. The substrate had nonideal structure, with the periodicity of four microns probably greater than that required, and had a resistivity of $10\Omega\cdot\text{cm}$, which was too low for accurate mobility measurements. Electrical and x-ray measurements at NJIT indicated that there was no pronounced difference in the samples and they were sent to Dr. Geis for further evaluation. The proposed NJIT research with etched structures will require higher resistivity Si and probably structures with smaller periodicity. Ken Braun at Raytheon Corporation offered to make x-ray exposed Au masks for exposure of photoresist with 1 micron patterns. Some difficulty in making these masks were encountered and it appears at this time that electron beam exposure of photoresist will be the approach used to make fine-line resist patterns. These photoresist patterns will be used to control hydrazene etching⁽¹⁰⁾ of Si with (100) surface orientation to form Vee slots with (111) sawtooth surfaces.

Progress was made in measuring the composition of deposited films with better than 1% accuracy using electron microprobe analysis (WDS) and by optical absorption measurements. A large number of theoretical optical absorption curves based on the analysis by Anderson⁽¹²⁾ are being calculated using the computer. These curves will be for different x values, temperature, and carrier concentration and type. They will be used for comparison with the experimental data obtained on sputtered thin film samples.

Film analysis work continues, with emphasis on determining the influence of the possible factors that can control the carrier concentration, mobility and lifetime of as-deposited and annealed sputtered films. Such factors include grain boundary scattering and charge trapping effects, surface scattering (related to film thickness), surface charge effects that may cause type-inversion and effectively decrease the film thickness (related to surface chemical treatment), and effects due to impurities and off-stoichiometry defects.

4.0 References

1. R.H. Cornely, L. Suchow, T. Gabara, and P. Diodato, "RF Triode-Sputtered Mercury Cadmium Telluride Thin Films," IEEE Transactions on Electron Devices, Vol. ED-27, 1, 1980, pp. 29-32.
2. R.H. Cornely, L. Suchow, M. Mulligan, R. Haq, "Properties of rf Triode-Sputtered $(Hg_{1-x}Cd_x)Te$ Thin Films," Proceedings of the Infrared Materials Session of the Society of Photo-Optical Instrumentation Engineer's Symposium East on April 21-24, 1981 in Washington, D.C.
3. M.A. Kinch, S.R. Borrello, B.H. Breageole, A. Simmons, "Geometrical Enhancement of $HgCdTe$ Photoconductive Detectors," Infrared Physics, Vol. 17, 1977, pp. 137-145.
4. U. Solzbach, and H.J. Ruhter, "Sputter Cleaning and Dry Oxidation of Cadmium Telluride, Mercury Telluride, and Mercury Cadmium Telluride $(Hg_{0.8}Cd_{0.2})Te$ Surfaces," Surf. Sci. 97(1), 1980, pp. 191-205.
5. R. Roussille, "Structural Properties of As Grown $Cd_xHg_{1-x}Te$ Epitaxial Layers Deposited by Cathodic Sputtering", NATO CMT Workshop, April 23-24, 1981 in Grenoble, France at LETI/LIR.
6. R.M. Finne and D.L. Klein, "A Water Amine Complexing Agent System for Etching Silicon", J. of the Electrochemical Society, 144, 1967, pp. 965.
7. M.J. Declercq, L. Gergberg, and J.D. Meindl, "Optimization of the Hydrazine-Water Solution for Anisotropic Etching of Silicon in integrated Circuit Technology" J. Electrochem. Society. 122 April, 1975, p. 545-552.
8. M.W. Geis, D.C. Flanders, and Henry I. Smith, "Grapho-Epitaxy of Silicon on Fused Silica using Surface micropatterns and Laser Crystallization", J. Vac Sci. Technol. 16 (6), Nov./Dec. 1979, p. 1640.
9. Private Communication with M.W. Geis on November 3, 1980.
10. A. B. Glaser and G.E. Subak-Sharpe, Integrated Circuit Engineering, Addison-Wesley, 1977, pp. 263-265.
11. M.D. Blue, "Optical Absorpriton in $HgTe$ and $HgCdTe$," Physical Review, Vol. 134. (1A), 2 pp. A226-A234. 1964. also Scott, M.W., "Energy Gap in $Hg_{1-x}Cd_xTe$ by Optical Absorption," Journal of Applied Physics, Vol. 40 (10), 1969, pp. 4077-81.
12. W.W. Anderson, "Absorption Constant of $Pb_{1-x}Sn_xTe$ and $Hg_{1-x}Cd_xTe$ Alloys," Infrared Physics, Vol. 20, 1980, pp. 363-72.
13. J.L. Schmidt, E.L. Stelzer, "Temperature and Alloy Compositional Dependences of the Energy Gap of $Hg_{1-x}Cd_xTe$," Journal of Applied Physics, Vol. 40, 1969, p. 4865.

5.0 Interactions and Publications

The following oral technical presentation were made during the 1980-81 grant period:

- 1) "The Effects of Annealing in Hg Vapor on the Properties of rf Sputtered Thin Films of $(Hg_{1-x}Cd_x)Te$ " by R. H. Cornely, L. Suchow, T. Chan, M. Mulligan, R. Haq, and C. Mehta presented at the Thin Films Session on Sputtering and Ion Beam Deposition at the American Vacuum Society's 27th National Symposium in Detroit on October 14, 1980.
- 2) "Properties of rf Triode-sputtered $(Hg_{1-x}Cd_x)Te$ Thin Films" by R. Cornely, M. Mulligan, and R. Haq was given at the Society of Photo-optical Instrumentation Engineer's Symposium East (SPIE-East) in Washington, D.C. on April 24, 1981.

The following publications during the 1980-81 grant period resulted from the research of this grant:

- 1) R. H. Cornely, L. Suchow, T. Chan, M. Mulligan, R. Haq, C. Mehta, "The Effects of Annealing in Hg Vapor on the Properties of rf Sputtered Thin Films of $(Hg_{1-x}Cd_x)Te$ ", Journal of Vacuum Science and Technology, vol. 18, No. 2, March 1981, pp. 190-194.
- 2) R. H. Cornely, L. Suchow, M. Mulligan, R. Haq, "Properties of rf Triode-Sputtered $(Hg_{1-x}Cd_x)Te$ Thin Films, Proceedings of the Infrared Materials Session of the Society of Photo-Optical Instrumentation Engineer's Symposium East on April 21-24, 1981 in Washington, D. C.

Dr. Cornely has interacted with numerous people involved with either thin film research related to this grant or $(Hg,Cd)Te$ material and devices.

Most important interactions are listed below.

- 1) Ted Harmon of Lincoln Labs discussed $(Hg,Cd)Te$ thin film research in several phone conversations and at the SPIE East Symposium. His experience with LPE grown $(Hg,Cd)Te$ films was very valuable for consultation on the sputtered film research, particularly for verifying the possible annealing temperatures and pressures that can yield good films.
- 2) Dr. Richard Schooler, the group leader of the Sensor Physics Section at the Aerospace Corporation, visited the NJIT laboratory for several hours. He was interested in learning about the sputtering research program and in meeting potential employees in $(Hg,Cd)Te$ work at Aerospace Corporation. The Air Force sponsored thin films program was discussed in detail along with some mutual problems, particularly the need for basic information on $(Hg,Cd)Te$ [such as absorption versus composition, absorption versus carrier concentration, and mobility versus impurity concentration] that remains unknown or unpublished by $(Hg,Cd)Te$ device manufacturers and scientists. He also was particularly interested in our research of ion-bombardment effects on $(Hg,Cd)Te$ and its meaning with respect to measuring composition. He sent NJIT information that pointed out that for high-density photoconductor arrays a lower mobility material, as we have obtained for as-deposited sputtered films, may

actually yield better device characteristics (due to a carrier-sweepout effect) than higher mobility material.

- 3) Valuable consultations were held with Irvin Kudmen and Valery Belov of Infrared Associates, New Brunswick, N. J. Dr. Belov, a recent immigrant from the Soviet Union where he was a Professor of Physics, had considerable experience with diffusion in semiconductors, particularly CdTe and (Hg,Cd)Te.
- 4) Several discussions were had with Esther Krikorian of General Dynamics concerning her reported research results on (Hg,Cd)Te thin films on CdTe substrates. Reported at the AVS meeting in Detroit.
- 5) At the October AVS meeting in Detroit, Dr. Cornely met Michael Geis of Lincoln Labs., who has been actively working for several years on graphoepitaxy. He agreed to send sample of Si with etched surface structure. Films of (Hg,Cd)Te were sputtered on the substrates, which unfortunately are of low resistivity, and evaluated at NJIT and Lincoln Labs. for enhancement of as-deposited grain size.
- 6) Another interaction was a rather long telephone conversation with Mr. Y. P. Lai of Varo, Inc. He had, read our IEEE Transactions article and is actively interested in starting his own program in sputtered (Hg,Cd)Te thin films. He was sent our latest film results.
- 7) An additional interaction is with Mr. Ken Braun, a former student at NJIT who is in charge of Raytheon's submicron device technology facility. He will help NJIT fabricate Si substrates with etched surface features on high resistivity Si substrates with etched surface features on high resistivity Si substrates.
- 8) Dr. E. Wiener-Avnear, senior scientist at Hughes Aircraft Co., discussed the NJIT (Hg,Cd)Te sputtering research for several hours at the AVS Detroit Symposium. He was sent copies of theses and published papers on NJIT's (Hg,Cd)Te research.
- 9) U. Solzbach of the Fraunhofer-Inst. Angew. Festkoerperphys., Freibruy, Fed. Rep. of Germany responded to an NJIT inquiry regarding his ESCA research of argon-bombarded (Hg,Cd)Te material and the growth of oxides on (Hg,Cd)Te.
- 10) Dr. Albert Tien, Nitec Corporation (312-647-7702-X284) contacted Dr. Cornely by telephone and requested information on the (Hg,Cd)Te sputtering research.
- 11) Dr. J. Schmidt of Honeywell Corp., Minneapolis, Minn. kindly lent NJIT a set of pieces of (Hg,Cd)Te material with known x values about 12 pieces of $(Hg_{1-x}Cd_x)Te$ material with different x values. These standards were used to determine the accuracy of electron microprobe measurements made at Structure Probe, Metuchen, N.J.

6.0 LIST OF PERSONNEL IN 1980-1981 GRANT

Dr. Roy H. Cornely: Principal Investigator, Associate Professor of Electrical Engineering, N.J.I.T., Director of Microelectronics Thin Films Laboratory.

Dr. Lawrence Suchow: Advisor, Full Professor in Department of Chemical Engineering and Chemistry, N.J.I.T.

Mr. Irwin Kudman: Advisor, President of Infrared Associates, New Brunswick, N.J.

Mr. Michael Mulligan: Graduate Student in Electrical Engineering, half-time academic year 1980-81, two months Summer 1980. Graduate Student Assistantship from AFOSR Grant for 80-81 Academic Year. Worked part-time as a Undergraduate Research Assistant for (Hg,Cd)Te Research from Jan. 1978 until June, 1980. Scheduled to finish MSEE thesis by October, 1981.

Mr. Robert Bourne: Graduate Student in Electrical Engineering, half-time academic year 1979-81, two months Summer 1979 and 1980. Graduate Assistantship from Army Research Office Grant for 79-80 and 80-81 Academic years.

Mr. Tai-On Chan: Graduate Student in Electrical Engineering, part-time academic year 79-80, 80-81, two months Summer 1980. Graduate Assistantship from AFOSR Grant in 1979-80. Scheduled to finish MSEE thesis by October, 1981.

Mr. Riaz Haq: Graduate Student in Electrical Engineering, part-time work on (Hg,Cd)Te Sputtering Research from October 1979 - April 1981. Scheduled to finish MSEE thesis by Augsut, 1981.

Mr. Chia-jen Wu: Graduate Student in Electrical Engineering. Began to work on (Hg,Cd)Te research in Jan. 1981. Scheduled to finish MSEE thesis by October, 1982.

Mr. Chet Mehta: Worked full-time as a Undergrad. Research Assistant in the Summer of 80 and 10 hours per week during the 80-81 Academic year.

Five other undergraduates worked as part-time laboratory assistants and two undergraduates did their senior projects on work related to the (Hg,Cd)Te thin film research.

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